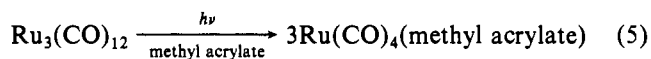


Reaction 1 does occur in CCl_4 with a quantum yield ca. 20 times greater than for reaction in the absence of CO. It seems somewhat improbable that reaction with quite low concentrations of CO, leading to fission of a Ru-Ru bond in the diradical, should be more rapid than chlorine abstraction from the CCl_4 solvent. The existence of a diradical intermediate should, therefore, not be assumed without question and non-radical, reactive isomeric forms of $\text{Ru}_3(\text{CO})_{12}$ (e.g., II) can easily be postulated. Reaction of II with CO to form $\text{Ru}_3(\text{CO})_{13}$ followed by rapid fragmentation is not unreasonable to contemplate. Similar processes have been proposed to occur during the thermal fragmentation reactions of $\text{Co}_4(\text{CO})_{12}$ ⁵ and $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ ¹¹ as well as in reactions of dinuclear complexes.¹²

The values of ϕ_{obsd} for reaction in isooctane under 100% CO show no perceptible dependence on irradiation wavelength. The values of ϕ_1 are necessarily less precise than those of ϕ_{obsd} because of the extrapolation involved, but those obtained for isooctane are also consistent with a wavelength-independent value of 0.065 ± 0.006 obtained from the weighted average of the three individual values. Similar wavelength independence is shown in cyclohexane and benzene. The limiting quantum yield for reaction 5 has been found to be over 3 times



higher when $\lambda = 313$ nm than when $\lambda = 395$ nm, and this enhanced value was ascribed to photochemically induced dissociation of CO.¹³ Our studies show that 313-nm excitation can lead to formation of a reactive isomeric form of $\text{Ru}_3(\text{CO})_{12}$ such as I or II, the additional CO dissociative process being reversed in the presence of free CO.

The solvent dependence of the reaction can best be indicated by the relative values of the parameter $\phi_1(k_f/k_r)$, which is equal to the initial slope of the plot of ϕ_{obsd} against $[\text{CO}]$. These fall in the relative order isooctane (100) > cyclohexane (90) > Decalin (30) > benzene (3). It is not obvious from these data whether the variation is due to a solvent dependence of ϕ_1 or k_f/k_r or both, but we believe that it is most likely to be due to a dependence on k_f/k_r . This represents a chemical selectivity on the part of the reactive intermediate as opposed to what is more likely to be a photophysical selectivity if ϕ_1 were solvent dependent. This is supported by data for reaction with other ligands.^{13,14}

Finally, the data in Table I suggest that there is a dependence of ϕ_1 on the nature of the attacking nucleophile. The weighted average of 0.065 ± 0.006 for ϕ_1 in isooctane over the range $\lambda = 313$ -436 nm can be compared with the value of 0.038 ± 0.002 for methyl acrylate in hexane with $\lambda = 395$ nm¹³ or 0.031 for ethyl acrylate in benzene with $\lambda = 436$ nm.¹⁴ This is of interest since it cannot readily be explained by a simple competitive reaction of a single reactive intermediate. In that case ϕ_1 would be reached when the reaction was driven in the forward direction every time the intermediate was formed (i.e., $k_f[\text{L}] \gg k_r$) and ϕ_1 would then be independent of the nature of the ligand. This aspect of the photochemical behavior is receiving further attention.

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Registry No. $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{Ru}(\text{CO})_5$, 16406-48-7; CO, 630-08-0; cyclohexane, 110-82-7; isooctane, 540-84-1; Decalin, 91-17-8; benzene, 71-43-2.

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Antiferromagnetic Ruthenium(III)

Sir:

We report here what appears to be the first example of antiferromagnetism in a discrete ruthenium(III) coordination compound, chloropentaammineruthenium(III) chloride, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

The high-temperature susceptibility of this compound has been reported¹ and shows that this $4d^5$ compound is low spin. That means, according to Bleaney and O'Brien,² that the ground state in the temperature range of our measurements (below 4.2 K) therefore should be an effective $S = 1/2$ ground state with anisotropic g values. Introducing the axial crystal field splitting parameter v and spin-orbit parameter ζ (which is estimated to be of the order of 1000 cm^{-1}), one calculates that

$$g_{\parallel} = 2|(1+k)\cos^2\alpha - \sin^2\alpha|$$

$$g_{\perp} = 2|2^{1/2}k\cos\alpha\sin\alpha + \sin^2\alpha|$$

where $\tan 2\alpha = 2^{1/2}(1/2 - v/\zeta)^{-1}$ and k is the orbital reduction factor; the latter is generally expected to take a value slightly smaller than 1. One can see from the relationships for the g values that they can be quite anisotropic and differ widely in value from compound to compound, depending on the local crystalline field. This can in turn lead to highly anisotropic magnetic ordering phenomena. EPR measurements at 77 K of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ doped into $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ have yielded³ the results that $g_x = 0.987 \pm 0.008$, $g_y = 1.513 \pm 0.005$, and $g_z = 2.983 \pm 0.003$, or an average value of 2.013. These results were shown to be consistent with the presence of a well-isolated doublet ground state.

The compound was prepared according to the method of Fergusson and Love⁴ and is known to belong to the space group $Pnma$.⁵ It is isostructural⁶ with $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and contains four molecules in the orthorhombic unit cell. Thus, there are two pairs of magnetically inequivalent complex ions in the cell. Further implications of the crystal structure for the magnetic properties were discussed in the report³ on the EPR spectra. The zero-field magnetic susceptibility of polycrystalline $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, measured by an ac mutual inductance procedure,⁷⁻⁹ is illustrated in Figure 1. For comparison,

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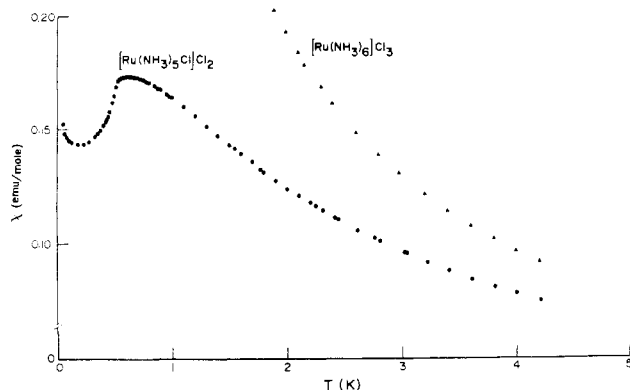
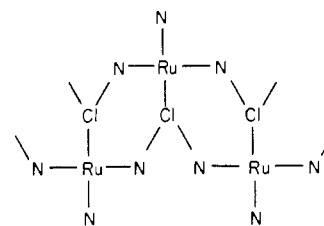


Figure 1. Zero-field magnetic susceptibilities of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (●) and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ (▲).

the susceptibility of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ is also included in the figure. The data for the latter compound obey the Curie-Weiss law over the temperature interval 1.1–4.2 K with the parameters $\langle g \rangle = 2.04 \pm 0.01$ and $\Theta = -0.036 \pm 0.05$ K, with the assumption of an effective $S = 1/2$ system. Paramagnetic behavior is expected to low temperatures; this is consistent with the presence of six ammonia ligands, which would not be expected to provide an important superexchange path, on the ruthenium(III) atom.

The data on $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ obey the Curie-Weiss law over the interval 2–4.2 K with $\langle g \rangle = 2.112 \pm 0.005$ and $\Theta = -1.36 \pm 0.05$ K. The g value is in satisfactory agreement with the average value of the g measured by EPR. The larger magnitude of Θ , which was assumed to be due to a measurable magnetic exchange interaction, caused us to measure the susceptibility to lower temperatures. The data go through a broad maximum at about 0.62 K and then drop at lower temperatures; the increase at the lowest temperatures is probably due to impurities. No out-of-phase signal was observed. This behavior is consistent with the onset of antiferromagnetic order;¹⁰ the transition temperature, estimated from the maximum slope in the data, is 0.525 ± 0.015 K. The replacement of only one ammine ligand by chloride, which was expected to enhance the superexchange interaction, has indeed led to magnetic ordering at an accessible temperature. The ordering temperature is low enough to suggest that the superexchange path is a weak one, but analysis of the crystal

structure^{5,6} suggests that there are three principal but inequivalent superexchange paths along each of the crystallographic directions. The suggested path is through $\text{Ru}-\text{NH}_3 \cdots \text{Cl}-\text{Ru}$ moieties with $\text{Ru}-\text{Ru}$ separations of 6.54–6.76 Å; hydrogen bonding between the NH_3 and Cl groups would tend to enhance the interaction. The strongest path appears to be along the b axis with "zigzag" double bridges of the form



with an $\text{Ru}-\text{Ru}$ distance of 6.54 Å. This structure suggests, potentially, a linear-chain magnetic interaction but with an important three-dimensional crossover¹¹ that leads to three-dimensional ordering at low temperatures. All the distances are long enough to preclude a relatively strong interaction as seen from the susceptibility measurements.

Lacking single-crystal measurements at this time, we have made no attempt to fit the data to one of the several magnetic model systems that are available.¹⁰ Efforts are under way to prepare such single crystals, as well as attempts to find more examples of ordered ruthenium(III) compounds. Studies on an isostructural series of iron(III) and ruthenium(III) compounds should be particularly illuminating if the iron compounds are high-spin, $S = 5/2$, isotropic systems while the ruthenium materials are low-spin, $S = 1/2$, potentially anisotropic compounds.¹²

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